XVIII.

NOTES ON THE OXIDES CONTAINED IN CERITE, SAMARSKITE, GADOLINITE, AND FERGUSONITE.

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In the present paper I have brought forward a number of observations and analyses which I hope will be of service to those who are engaged in the study of the rarer earths. The subject is one of such extreme difficulty, that even the results of an imperfect study may have value.

For the material which I have employed I have been chiefly indebted to Dr. Waldron Shapleigh, Chemist to the Welsbach Incandescent Light Company, by whom I have been liberally supplied with various preparations in a state of considerable purity. I have also to make my acknowledgments to Professor Everhart, from whom I have received a considerable quantity of gadolinite from the well known locality in Llano County, Texas. The material given me by Dr. Shapleigh consisted in part of beautiful crystalline double nitrates of the earths and ammonium, and in part of crude oxides. The double nitrates contained only the earths present in cerite, and for the most part only Ce_2O_3, Ln_2O_3, Ps_2O_3, and Nd_2O_3, with very small relative quantities of Y_2O_3, and traces only of other earths. In converting the crude oxides into sulphates it is best to sift the fine powder slowly upon the surface of cold dilute sulphuric acid. The sulphates are then formed at once as fine crystalline powders free from hard lumps. Another method sometimes applicable with advantage consists in mixing the oxides with an excess of ammonic sulphate, and then igniting slowly in porcelain crucibles, which are to be heated in a muffle to low redness until vapors are no longer given off. The sulphates then present a beautiful snow-white soft crystalline powder, and readily form saturated solutions with cold water. In all work with the rare earths, oxalates from their insolubility play a very important part. They may, as all chemists know, be readily converted into sulphates by treatment with sul-

phuric acid and careful expulsion of the excess of this last by heat. I have found it more convenient to mix the oxalate intimately with an excess of ammonic sulphate and heat carefully in a muffle, as in the last case. The resulting sulphates are perfectly soluble without packing together if sifted upon the surface of cold water. They are also perfectly neutral. The oxalates may also be converted into chlorides by mixing them intimately with ammonic chloride and igniting the mixture in a muffle very gently.

Determinations of mean atomic mass are now always employed in the study of the mixtures of oxides which present themselves in the attempt to effect separations. Very accurate results are obtained by the usual method of converting a weighed quantity of oxides into the equivalent weight of sulphates by treatment with sulphuric acid and subsequent careful ignition. Probably this could be done more conveniently, and in less time, by igniting the oxides in porcelain crucibles in a muffle, after mixing carefully with ammonic sulphate, but upon this point I have made no quantitative experiments.

In all my work I have employed the analysis of the oxalates as convenient and accurate. It is, however, necessary to insist upon several points of detail. In the first place I remark that the preparation of perfectly homogeneous mixtures of the oxalates requires much care. It is best to precipitate by a hot dilute solution of oxalic acid added slowly in small but distinct excess to a hot dilute solution of the mixed chlorides or nitrates. The precipitated oxalates are then to be thoroughly washed by decantation with hot distilled water. This requires in general a large quantity of water, and must be continued until the washings contain no trace of oxalic acid and give no cloudiness with ammonia. Auer von Welsbach's process, which consists in adding a very dilute solution of the nitrates (or chlorides) to a hot dilute solution of oxalic acid, gives the oxalates in a state of very fine subdivision and perfectly free from hard masses. The mixed washings on saturation with ammonia sometimes give a precipitate of oxalates, though in small quantity. These oxalates may be washed and mixed with the main portion. The mass is to be dried upon a water-bath, and then thoroughly mixed in a dry mortar. Only in this manner is it possible to obtain a mass of oxalates sufficiently homogeneous to yield corresponding results when different portions are analyzed. The determination of the mean atomic mass in the oxalates prepared as above involves only the determination of the percentages of oxide R_2O_3 and of C_2O_3, the water present being of course without influence. Here I may remark that, as has doubtless been observed by other

chemists, the last portions of water require a very high temperature for expulsion. The details of the method which I employ are as follows. From 0.5 gr. to 1 gr. of the oxalate is to be gently heated until the greater part of the water and carbonic dioxide have been driven off, and then at a full red heat for fifteen to twenty minutes with a blast lamp to a constant weight. During ignition the crucible is best placed at an angle, and partly uncovered to permit free access of air. The mixed oxides do not retain a weighable amount of carbonic dioxide. To determine C_2O_3, from 0.3 gr. to 0.4 gr. of the oxalate are to be weighed into a 250 c.c. flask; 20 c.c. of water and 30 c.c. of dilute sulphuric acid, 1 : 6 by volume, are then to be added and the flask is to be gently heated upon a sand-bath until the solution is complete, when the hot liquid is to be titrated with carefully standardized permanganate. The following analyses will show the correspondence between the results obtained by the above described method and those obtained by the sulphate process. In an oxalate from a perfectly colorless nitrate of lanthanum and ammonium sent me by Dr. Shapleigh, —

(1)	0.3344 gr.	gave	0.1009 gr. C_2O_3	= 30.15	per cent.
(2)	0.3274 gr.	"	0.09895 gr. "	= 30.07	"
(3)	0.3726 gr.	"	0.1120 gr. "	= 30.08	"
(4)	0.3485 gr.	"	0.1050 gr. "	= 30.11	"
(5)	0.5931 gr.	"	0.2706 gr. R_2O_3	= 45.61	"
(6)	0.5977 gr.	"	0.2728 gr. "	= 45.64	"

The means are 30.10 per cent C_2O_3, and 45.625 per cent R_2O_3. The mean atomic mass calculated from the above is 139.70. Dr. Shapleigh found by the sulphate method 139.75, 139.72, 139.67, mean 139.71.

The necessity of thoroughly mixing the oxalates will appear from the following analyses made with oxalates simply washed and dried: —

(7)	0.3549 gr.	gave	0.1274 gr. C_2O_3	= 35.88	per cent.
(8)	0.3697 gr.	"	0.1316 gr. "	= 35.59	"
(9)	0.3807 gr.	"	0.1382 gr. "	= 36.29	"
(10)	0.6550 gr.	"	0.2869 gr. R_2O_3	= 43.79	"
(11)	0.6125 gr.	"	0.2699 gr. "	= 44.07	"

The same oxalates carefully mixed in a mortar were also analyzed for comparison: —

(12) 0.3357 gr. gave 0.1213 gr. C_2O_3 = 36.16 per cent.
(13) 0.3856 gr. " 0.1393 gr. " = 36.13 "
(14) 0.6538 gr. " 0.2906 gr. R_2O_3 = 44.45 "
(15) 0.7074 gr. " 0.3145 gr. " = 44.46 "

The analyses leave no doubt whatever as to the necessity of carefully mixing the precipitated oxalates. They also show that in determinations of atomic mass by the sulphate method both oxalates and oxides should be well ground up to secure homogeneity. It has been shown that the oxalate and sulphate methods executed with proper care give equally accurate results. Each has its advantages, and in this respect there is but little choice. As the study of the rarer earths as now conducted usually depends more or less upon the properties of the double salts which they form with potassic and sodic sulphates, it may be well to call attention to facts not, I believe, noticed in printed papers, though doubtless recognized. The first is that the earths in the double sulphates may be converted directly into oxalates by boiling the sulphates with chlorhydric and oxalic acids, and then diluting with much water. The second fact is that oxalates obtained in this way, as from any alkaline solutions, should always be converted into oxides by ignition. These should then be dissolved in chlorhydric acid, again precipitated by oxalic acid, and the oxalates thoroughly washed.

In determining atomic masses by either the sulphate or oxalate method, the assumption is tacitly made that all the oxides taken for analysis are of the type R_2O_3. This is not true when cerium is present, as in that case a portion at least of this metal is present as CeO_2 after ignition. Higher oxides than R_2O_3 are also present to some extent, at least when praseodymia and neodymia are mixed with ceria, or even when this last oxide is not present. Ceric oxide is not reduced by a full red heat to cerous oxide, or even by a current of hydrogen, at least in a crucible. The error committed is not, however, large when we consider the cerium as Ce_2O_3 instead of Ce_2O_4, and is still less in the cases of the other oxides. When great accuracy is necessary, it may be well to remove the four cerite oxides by means of potassic or sodic sulphate before determining the atomic mass.

In a number of analyses I determined the percentage of oxides by simply igniting the oxalate with a weighed quantity of pure sodic tungstate. This method gives very accurate results, but, as pure sodic tungstate must always be specially prepared in the laboratory, is not to be greatly recommended. Ceric oxide is not reduced

to cerous oxide by heating with the tungstate to a red heat for some time. I may here state that a test for ceria more delicate than that which I gave many years since (PbO_2 and NO_3H) is obtained by employing the oxide of bismuth, Bi_2O_4, in place of plumbic oxide.

With these preliminaries I proceed to special methods of separating the mixed oxides. A series of experiments was first made to determine to what extent differentiation is effected by successive partial precipitations by oxalic acid. The method is of course not new, but, so far as I know, it has not been tested by quantitative analyses, and no attempt has been made to determine the rate of change. The material used in this case was a mixture of sulphates, the sulphate of neodymium being present in largest quantity. Thoric and other oxides in less quantity were also present. The material was obtained from Dr. Shapleigh in the form of oxides. After careful purification the atomic mass of the oxides was first determined: —

(16)	0.5622 gr.	gave	0.1715 gr.	C_2O_3	=	30.50	per cent.
(17)	0.4782 gr.	"	0.1458 gr.	"	=	30.50	"
(18)	0.4355 gr.	"	0.1326 gr.	"	=	30.47	"
(19)	0.6100 gr.	"	0.2778 gr.	R_2O_3	=	45.55	"
(20)	0.6904 gr.	"	0.3141 gr.	"	=	45.50	"

The analyses give as the atomic mass 137.25. A portion of the oxides was then converted into sulphates, and the number of cubic centimeters of a solution of oxalic acid required for complete precipitation, determined by experiment with a sufficiently close approximation. A solution of the sulphates having a very fine rose-red color was then precipitated in five successive additions of equal volumes of a solution of oxalic acid. After each addition of the acid the resulting oxalate was filtered off and washed. The washings were then added to the filtrate. It will be seen that in this way the bulk of the solution increased before each precipitation after the first. The results are as follows: —

I.	(21)	0.3126 gr.	gave	0.0941 gr.	C_2O_3	=	30.52	per cent.
	(22)	0.3410 gr.	"	0.1042 gr.	"	=	30.54	"
	(23)	0.5773 gr.	"	0.2820 gr.	R_2O_3	=	48.84	"
	(24)	0.5856 gr.	"	0.2855 gr.	"	=	48.75	"

Atomic mass 148.60.

II.	(25)	0.3563 gr.	gave	0.1114 gr.	C_2O_3	= 31.26	per cent.
	(26)	0.3500 gr.	"	0.1091 gr.	"	= 31.20	"
	(27)	0.6848 gr.	"	0.3317 gr.	R_2O_3	= 48.43	"
	(28)	0.6664 gr.	"	0.3223 gr.	"	= 48.37	"
		Atomic mass 143.35.					
III.	(29)	0.3500 gr.	gave	0.1113 gr.	C_2O_3	= 31.78	"
	(30)	0.3127 gr.	"	0.09936 gr.	"	= 31.77	"
	(31)	0.6859 gr.	"	0.3345 gr.	R_2O_3	= 48.75	"
	(32)	0.7087 gr.	"	0.3447 gr.	"	= 48.65	"
		Atomic mass 141.55.					
IV.	(33)	0.3350 gr.	gave	0.1042 gr.	C_2O_3	= 31.12	"
	(34)	0.3410 gr.	"	0.1060 gr.	"	= 31.09	"
	(35)	0.6369 gr.	"	0.2958 gr.	R_2O_3	= 46.44	"
	(36)	0.6468 gr.	"	0.3004 gr.	"	= 46.45	"
		Atomic mass 137.25.					
V.	(37)	0.2042 gr.	gave	0.06864 gr.	C_2O_3	= 33.62	"
	(38)	0.2031 gr.	"	0.06828 gr.	"	= 33.62	"
	(39)	0.3045 gr.	"	0.1409 gr.	R_2O_3	= 46.26	"
	(40)	0.3400 gr.	"	0.1569 gr.	"	= 46.14	"
		Atomic mass 124.40.					

The filtrate from the last portion of oxalates contained only traces of earths. The analyses show that the earths with the highest atomic masses are precipitated first by oxalic acid. The average rate of decrease of mean atomic mass is five units for each operation, but the rate is by no means uniform. The results prove that precipitated oxalates must be very carefully mixed mechanically before analysis when more than one earth is present. The analyses also show that four fifths of the earths might have been precipitated at once by oxalic acid if the object had been to obtain yttria with the least outlay of time and labor, the atomic mass of the last fifth being 124.40.

Oxychlorides. — When the chlorides of the metals belonging to the cerium and yttrium groups, or, more generally stated, of the metals yielding the rarer earths, are carefully heated, oxychlorides are formed in greater or less proportion mixed with undecomposed chlorides. We may distinguish these as acid and basic chlorides. Water dissolves out the former very readily, and leaves nearly or quite colorless basic chlorides, which are, relatively at least, insoluble. I find that in this way the earths present are separated into two groups, and that by repeating the operation upon each group a second differentiation is

effected in each case. The process appears to deserve attention, and to compare very favorably with separation by means of basic nitrates. The details of this method are as follows.

The mixed oxides in as pure a state as possible are to be dissolved in a small excess of pure chlorhydric acid; the solution is then to be evaporated at first on a water-bath, and then on a sand-bath, until a thick syrup is obtained. This is to be transferred to a porcelain crucible, which is then to be heated gently in a muffle. The heat should not be allowed to exceed low redness. Much chlorhydric acid is given off during the heating, and a white mass remains which consists in part of a mixture of oxychlorides, and in part of unaltered chlorides. The mass is then to be treated with hot water in rather small portions at a time, the solution being poured off before each new addition. When the washing is nearly complete, the solution becomes turbid. The white insoluble mass and supernatant liquid are then to be evaporated to dryness, or to a thick syrup, after the addition of enough chlorhydric acid to effect complete solution. The liquid poured off and containing the soluble chlorides is also to be evaporated to dryness, but without addition of chlorhydric acid. We have then two separate portions, of which one, A, contains the soluble or relatively acid chlorides, and the other, B, the neutralized oxychlorides. Each of these portions is to be treated in the muffle as in the first case. In this manner two new basic chlorides, B_2 and B_3, and two new acid chlorides, A_2 and A_3, are obtained. The same processes are to be repeated as long as the material lasts. The atomic mass of the oxides taken must first be determined, and afterward the atomic masses of the portions A_1, A_2, A_3, etc., and B_1, B_2, B_3, etc. This enables us to determine the rate of change in the atomic masses produced by the successive operations. Of course it is only necessary to take a small portion of each product A_1, B_1, etc., for the determination of the atomic mass. The whole process will perhaps be rendered more clear by means of a diagram, and in illustration I shall select the results of actual work in a particular case. The starting point in this case was a mixture of oxides from Texas gadolinite having the atomic mass 107.5. The data are as follows: —

(41)	0.3577 gr.	gave	0.1357 gr.	C_2O_3	= 37.94	per cent.
(42)	0.3246 gr.	"	0.1228 gr.	"	= 37.81	"
(43)	0.3999 gr.	"	0.1515 gr.	"	= 37.86	"
(44)	0.6113 gr.	"	0.2814 gr.	R_2O_3	= 46.04	"
(45)	0.6670 gr.	"	0.3064 gr.	"	= 45.94	"
(46)	0.6303 gr.	"	0.2892 gr.	"	= 45.88	"

Atomic mass 107.5.

B_1 Left. Atomic mass 110.8.

(47) 0.6836 gr. gave 0.3289 gr. R_2O_3 = 48.11 per cent.
(48) 0.2344 gr. " 0.0904 gr. C_2O_3 = 38.57 "

A_1 Right. Atomic mass 94.75.

(49) 1.2740 gr. gave 0.4976 gr. R_2O_3 = 39.65 per cent.
(50) 0.2998 gr. " 0.1065 gr. C_2O_3 = 35.51 "

B_2 Left. Atomic mass 117.4.

(51) 0.4327 gr. gave 0.2157 gr. R_2O_3 = 49.84 per cent.
(52) 0.2860 gr. " 0.1089 gr. C_2O_3 = 38.07 "

A_2 Left. Atomic mass 98.35.

(53) 0.7897 gr. gave 0.3714 gr. R_2O_3 = 47.03 per cent.
(54) 0.3772 gr. " 0.1566 gr. C_2O_3 = 41.52 "

B_3 Left. Atomic mass 122.

(55) 0.5910 gr. gave 0.2803 gr. R_2O_3 = 47.43 per cent.
(56) 0.2023 gr. " 0.0710 gr. C_2O_3 = 35.09 "

A_3 Left. Atomic mass 102.8.

(57) 0.4472 gr. gave 0.2137 gr. R_2O_3 = 47.78 per cent.
(58) 0.3067 gr. " 0.1248 gr. C_2O_3 = 40.70 "

A_1 Right. Atomic mass 94.75.

(59) 1.2740 gr. gave 0.4976 gr. R_2O_3 = 39.05 per cent.
(60) 0.2998 gr. " 0.1065 gr. C_2O_3 = 35.51 "

A_2 Right. Atomic mass 91.65.

(61) 1.0032 gr. gave 0.3948 gr. R_2O_3 = 39.37 per cent.
(62) 0.5057 gr. " 0.1856 gr. C_2O_3 = 36.77 "

B_2 Right. Atomic mass 98.6.

(63) 0.7353 gr. gave 0.3291 gr. R_2O_3 = 44.75 per cent.
(64) 0.3343 gr. " 0.1318 gr. C_2O_3 = 39.43 "

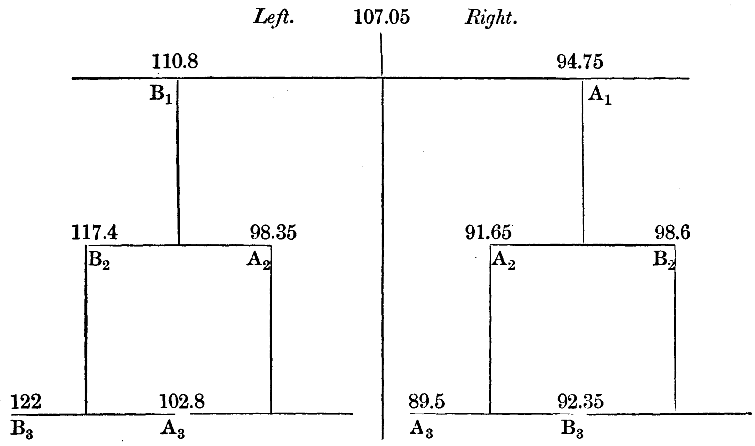
A_3 Right. Atomic mass 89.5.

(65) 0.4864 gr. gave 0.2146 gr. R_2O_3 = 44.12 per cent.
(66) 0.2212 gr. " 0.0929 gr. C_2O_3 = 42.00 "

B_3 Right. Atomic mass 92.35.

(67) 0.5183 gr. gave 0.2238 gr. R_2O_3 = 43.17 per cent.
(68) 0.2080 gr. " 0.0834 gr. C_2O_3 = 40.07 "

The following diagram enables us to take in all the results at a glance.



It must be noted that in the above and on the diagram, B_1, B_2, B_3, etc. denote basic or oxychlorides; A_1, A_2, A_3, etc., neutral or relatively acid chlorides. The analyses were not pursued further because the material taken was exhausted by the separations accomplished. The examination of the results obtained in this particular case by the basic chloride process leads to interesting conclusions. In the first place, it will be remarked that the atomic masses of the insoluble basic chlorides increase with each successive separation into basic and acid chlorides, while the neutral or relatively acid chlorides give diminishing atomic masses. In the cases of these last, three successive operations give a nearly pure yttria, with atomic mass 89.5. The rate of increase of the atomic masses of the successive portions B_1, B_2, B_3, is about 5.3 units for each operation. The rate of decrease of the portions A_1, A_2, A_3, is about 2.6 units for each operation. It is not to be expected that perfectly uniform results will be obtained even when the process is applied to the same mixture of oxides, because the amount of separation into basic and acid chlorides by each operation must depend very much upon the temperature of the muffle and the length of time during which the heat is applied. In the second place, it must be noted that, while a very nearly pure yttria is obtained in three operations, this does not represent the whole quantity of the earth in the compound. It will also be seen that a decided advantage must be secured by making mixtures of the products hav-

ing nearly the same atomic masses, and then applying the method of separation to these.

Other applications of the method give, as I will now show, substantially similar results. The next substance examined was a mixture of oxides received from Dr. Shapleigh, and obtained from residual mother liquors of cerite and monazite salts. The oxide was dissolved in chlorhydric acid, and purified by a current of sulphydric acid. Of the mixed oxalates, —

(69)	0.5622 gr.	gave	0.1715 gr.	C_2O_3	= 30.50	per cent.
(70)	0.4782 gr.	"	0.1458 gr.	"	= 30.50	"
(71)	0.4355 gr.	"	0.1326 gr.	"	= 30.47	"
(72)	0.6100 gr.	"	0.2778 gr.	R_2O_3	= 45.55	"
(73)	0.6904 gr.	"	0.3141 gr.	"	= 45.50	"

Atomic mass 137.25.

I also determined the mean atomic mass after separating the cerite earths by means of sodic sulphate in the usual manner. Of course some yttria went down with the double sulphates.

(74)	0.2440 gr.	gave	0.0946 gr.	C_2O_3	= 38.77	per cent.
(75)	0.2438 gr.	"	0.0946 gr.	"	= 38.80	"
(76)	0.4597 gr.	"	0.2146 gr.	R_2O_3	= 46.68	"
(77)	0.3570 gr.	"	0.1668 gr.	"	= 46.72	"

Atomic mass 106.05.

The oxides with atomic mass 106.05 were then treated by the oxychloride process.

Portion B_1 Left.

(78)	0.4027 gr.	gave	0.1505 gr.	C_2O_3	= 37.38	per cent.
(79)	0.5204 gr.	"	0.1943 gr.	"	= 37.35	"
(80)	0.6947 gr.	"	0.3250 gr.	R_2O_3	= 46.78	"
(81)	0.9233 gr.	"	0.4323 gr.	"	= 46.82	"

Atomic mass 111.3.

Portion B_2 Left.

(82)	0.4127 gr.	gave	0.1464 gr.	C_2O_3	= 35.49	per cent.
(83)	0.3215 gr.	"	0.1142 gr.	"	= 35.51	"
(84)	0.5885 gr.	"	0.2668 gr.	R_2O_3	= 45.33	"
(85)	0.6205 gr.	"	0.2814 gr.	"	= 45.35	"

Atomic mass 113.95.

Portion A_1 Right.

(86) 0.4332 gr. gave 0.1630 gr. C_2O_3 = 37.63 per cent.
(87) 0.3239 gr. " 0.1217 gr. " = 37.57 "
(88) 0.6813 gr. " 0.3062 gr. R_2O_3 = 44.94 "
(89) 0.6749 gr. " 0.3035 gr. " = 44.95 "

Atomic mass 105.1.

Portion A_2 Right.

(90) 0.3317 gr. gave 0.1161 gr. C_2O_3 = 35.02 per cent.
(91) 0.3216 gr. " 0.1126 gr. " = 35.00 "
(92) 0.6800 gr. " 0.2823 gr. R_2O_3 = 41.52 "
(93) 0.6529 gr. " 0.2709 gr. " = 41.50 "

Atomic mass 104.05.

B_2 Right.

(94) 0.3785 gr. gave 0.1314 gr. C_2O_3 = 34.73 per cent.
(95) 0.2882 gr. " 0.0999 gr. " = 34.68 "
(96) 0.6187 gr. " 0.2676 gr. R_2O_3 = 43.25 "
(97) 0.6421 gr. " 0.2770 gr. " = 43.24 "

Atomic mass 110.45.

A_2 Left.

(98) 0.3458 gr. gave 0.1290 gr. C_2O_3 = 37.31 per cent.
(99) 0.4089 gr. " 0.1523 gr. " = 37.24 "
(100) 0.6892 gr. " 0.3062 gr. R_2O_3 = 44.43 "
(101) 0.5986 gr. " 0.2660 gr. " = 44.44 "

Atomic mass 104.75.

A_3 Right.

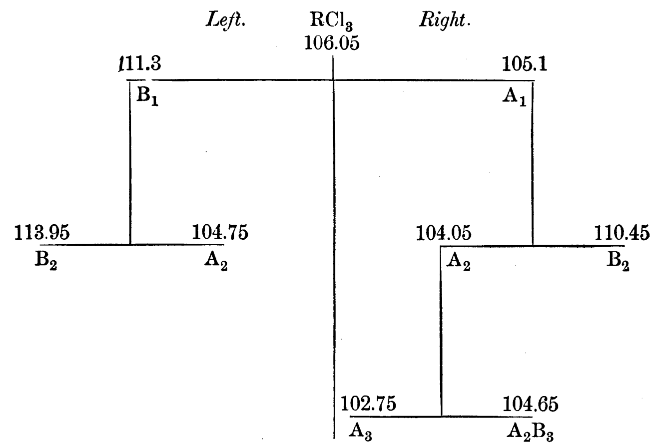
(102) 0.3002 gr. gave 0.1162 gr. C_2O_3 = 38.73 per cent.
(103) 0.3251 gr. " 0.1260 gr. " = 38.77 "
(104) 0.6667 gr. " 0.3031 gr. R_2O_3 = 45.44 "
(105) 0.7642 gr. " 0.3478 gr. " = 45.51 "

Atomic mass 102.75.

(106) A_2, B_3 Right.
(107) 0.3426 gr. gave 0.1307 gr. C_2O_3 = 38.16 per cent.
(108) 0.3401 gr. " 0.1298 gr. " = 38.18 "
(109) 0.8197 gr. " 0.3728 gr. R_2O_3 = 45.46 "
(110) 0.7623 gr. " 0.3467 gr. " = 45.47 "

Atomic mass 104.65.

These determinations exhausted the material employed. The following diagram brings together all the results.



The diagram in the case of the oxides from cerite and monazite shows very clearly that, as with the oxides from gadolinite, the atomic masses B_1, B_2, B_3 increase, while those of A_1, A_2, A_3 diminish, but at a different rate, perhaps, as already remarked, because the conditions were not precisely the same. It seems very desirable that similar experiments should be made with the basic nitrate process, which has been so much used, so as to determine which method gives results that converge most rapidly toward the atomic masses of pure oxides. Only in this manner can the relative values of the two methods be determined. I consider it probable that further experience with the oxychloride process will lead to a very material shortening of the process. I have employed for the most part porcelain crucibles holding about 130 c.c., but with larger muffles it would be easy to work up a kilogram of oxides at each operation. Also much is to be expected from a judicious mixture of the different products on the right and left having nearly the same atomic masses. All points fairly considered, I am I believe justified in offering the oxychloride process as worthy of further trial.

It appeared possible that basic bromides might be more advantageous than basic chlorides as means of differentiation, but the experiments made were not conclusive on this point. Observing the formation of beautiful well defined crystals when the oxides from gadolinite and the cerite and monazite residues were dissolved in chlorhydric or

bromhydric acid, and the solutions evaporated to a syrupy consistence, I examined two cases. The perfectly colorless and easily soluble crystals obtained from gadolinite earths free from cerite earths by chlorhydric acid after two successive crystallizations were analyzed.

(111)	0.3248 gr.	gave	0.1293 gr. C_2O_3	= 39.82	per cent.
(112)	0.3000 gr.	"	0.1450 gr. R_2O_3	= 48.34	"

The atomic mass is 107.10 so that the crystalline chlorides contained the earths in the same proportion in which they were obtained from gadolinite after separation of the cerite earths.

Precisely the same result was obtained with crystallized bromides prepared by dissolving the crude oxides from the cerite and monazite residues in bromhydric acid and evaporating. The beautiful colorless crystals were not quite free from the mother liquor. Of these crystals,

(113)	0.3418 gr.	gave	0.1064 gr. C_2O_3	= 31.11	per cent.
(114)	0.4266 gr.	"	0.1325 gr. "	= 31.07	"
(115)	0.6110 gr.	"	0.2879 gr. R_2O_3	= 47.13	"
(116)	0.6896 gr.	"	0.3293 gr. "	= 47.02	"

The atomic mass is 139.55, which is nearly the same as that obtained from the oxides directly, 137.25.

The mother liquor from the crystals was also analyzed.

(117)	0.3750 gr.	gave	0.1171 gr. C_2O_3	= 31.25	per cent.
(118)	0.3237 gr.	"	0.1015 gr. "	= 31.37	"
(119)	0.6752 gr.	"	0.3180 gr. R_2O_3	= 47.10	"
(120)	0.8150 gr.	"	0.3837 gr. "	= 47.08	"

The atomic mass corresponding is 138.45. From the above it appears that little, if anything, is gained by crystallization of the chlorides and bromides, at least in the cases cited.

The fact, that potassic and sodic sulphates which do not give precipitates of double sulphates in cold saturated solutions of certain earths often give crystalline precipitates on boiling, has doubtless been observed. I do not find, however, that such observations have been noted in published papers. The following analyses will serve to show that valuable results may sometimes at least be obtained by this process.

A quantity of oxides from Samarskite, sent me by Dr. Shapleigh, was dissolved in chlorhydric acid, and precipitated cold by an excess of potassic sulphate. After filtering off the double sulphates, sodic sulphate was added and the solution boiled. An abundant white crystalline salt was obtained. After washing with a little boiling water the double salt was dissolved in chlorhydric acid, and oxalic acid added after large dilution. The oxalates were converted into oxides and these redissolved in chlorhydric acid and again precipitated with oxalic acid. The oxalates were then analyzed.

(121)	0.2853 gr.	gave	0.1217 gr.	R_2O_3.
(122)	0.3889 gr.	"	0.1660 gr.	"
(123)	0.5558 gr.	"	0.2256 gr.	C_2O_3.

Atomic mass 89.55, which does not sensibly differ from the received atomic mass of yttrium. From this it appears that yttria was separated in quantity by one operation after the separation of the cerite oxides.

Application of the Cobaltamines to the Separation of the Oxides. — Many experiments were made to determine whether the sulphates of organic alkaloids would form double salts with the sulphates of the rare earths which could be made available for separations. These did not lead to satisfactory results, though double salts were formed in some cases. It then occurred to me that the sulphates and other salts of various cobaltamines, on account of their disposition to form highly crystalline compounds, might be employed with advantage. Following are the results of this investigation.

A solution of sulphate of luteocobalt precipitates completely from their cold solutions as neutral sulphates the four cerite earths now known, namely, the oxides of cerium, lanthanum, praseodymium, and neodymium. The double sulphates are beautifully crystalline, have an orange-red color, and are very slightly soluble in cold water, but practically at least insoluble in boiling water. They are soluble in acids, and sometimes crystallize from weak acid solutions. All these compounds appear to have the same constitution, which is that of the salts discovered many years since by myself, and analyzed in my laboratory by C. H. Wing.* I find, however, that the constitution of both the luteo- and roseo-salts may be much more accurately represented by the formulas:

* American Journal of Science and Art, XLIX. [2.] 363.

$$\text{I.}\quad 2\{Co_2(NH_3)_{12}(SO_4)_3 + Ce_2(SO_4)_3\} + 3\text{ aq.}$$
$$\text{II.}\quad 2\{Co_2(NH_3)_{12}(SO_4)_3\} + 3\{Ce(SO_4)_2\} + 3\text{ aq.}$$
$$\text{III.}\quad 2\{Co_2(NH_3)_{10}(SO_4)_3 + Ce_2(SO_4)_3\} + 9\text{ aq.}$$
$$\text{IV.}\quad 2\{Co_2(NH_3)_{10}(SO_4)_3 + 3\{Ce(SO_4)_2\} + 9\text{ aq.}$$

Mr. W. J. Karslake has arrived independently at the same formulas, and has calculated the percentages as required by them.

For Formula I.

		Calculated.	Found.
24 NH_3	408	16.93	16.75 (loss)
4 Co	236	9.79	9.31
4 Ce	560	23.24	24.10
12 SO_4	1152	47.80	47.77
3 H_2O	54	2.24	2.07
	2410	100.00	

For Formula II.

		Calculated.	Found.		
24 NH_3	408	17.97	17.73 (loss)		
4 Co	236	10.40	10.80	10.74	10.44
3 Ce	420	18.57	16.90	17.27	17.54
12 SO_4	1152	50.75	51.80	51.83	52.22
3 H_2O	54	2.37	2.47	2.21	2.39
	2270	100.00			

For Formula III.

		Calculated.	Found.	
20 NH_3	340	14.72	14.24 (loss)	
4 Co	236	10.22	10.39	9.60
3 Ce	420	18.18	18.18	19.36
12 SO_4	1152	49.86	49.73	49.97
9 H_2O	162	7.02	7.00	7.31
	2310	100.00		

For Formula IV.

		Calculated.	Found.
20 NH_3	340	13.88	15.13 (loss)
4 Co	236	9.64	9.90
4 Ce	560	22.85	20.99
12 SO_4	1152	47.02	47.23
9 H_2O	162	6.61	6.75
	2450	100.00	

The analyses are those of Wing. Recent determinations of the molecular masses of the cobaltamines have shown that the chlorides,

for example, of roseocobalt and luteocobalt are represented respectively by the formulas $Co(NH_3)_5Cl_3$ and $Co(NH_3)_6Cl_3$. I have kept the old formulas only to permit an easy comparison with those given by Wing, and the matter is not one of consequence in this place. It may also be remarked that, as cerium is at present the only one of the group which forms a well defined oxide higher than R_2O_3, the two formulas II. and IV. cannot be generalized by substituting the symbols of other elements for that of cerium. I have endeavored, however, to prepare such compounds by adding a solution of $Lc_2(SO_4)_3$ to one containing the sulphates of oxides other than the cerite oxides, and then adding some oxidizing agent, as for instance potassic permanganate, chlorine, or bromine. No decisive results were obtained. It is at least probable that all the earths the sulphates of which in cold solutions give only slightly soluble double sulphates with potassic and sodic sulphates will also give insoluble double sulphates with sulphate of luteocobalt. These earths are, so far as now known, Ce_2O_3, La_2O_3, Nd_2O_3, Ps_2O_3, Sm_2O_3, Sc_2O_3, while the following give soluble double sulphates: Er_2O_3, Y_2O_3, Yb_2O_3, and Tb_2O_3. The four cerite oxides cited are not the only ones which give insoluble crystalline precipitates with sulphate of luteocobalt in the cold, but I am not at present able to give more accurate information on this point. On the other hand, we meet in the case of luteocobalt sulphate with some of the relations which present themselves when the alkaline sulphates are employed. Thus sulphate of yttria is not precipitated by sulphate of luteocobalt when alone, but when mixed with the sulphates of the cerite group more or less of a double sulphate of luteocobalt and yttria is always thrown down, and the same appears to be true for the sulphates of some other earths. In such cases the mixed sulphates of earths and luteocobalt should be gently heated in a muffle until the cobaltamine is completely decomposed and the excess of sulphuric acid is expelled. The residual sulphates of cobalt and the earths should then be dissolved in cold water, filtered, and again precipitated by sulphate of luteocobalt, allowing the mixture to stand twenty-four hours. The supernatant liquid appears then to contain all but the four cerite earths. This point is, however, not yet sufficiently proved, and I reserve it for further investigation.

The solution from which the double sulphates of the cerite earths and luteocobalt have been separated by decantation or filtration usually gives a more or less abundant crystalline precipitate on boiling. The filtrate from this again gives a precipitate with ammonia. The above stated facts are precisely those which we meet with in employing

the alkaline sulphates in place of the sulphate of luteocobalt. I have also employed the sulphato-chloride of luteocobalt, $Lc_2(SO_4)_2Cl_2$, as a precipitant, and find that double salts are sometimes formed which are much more insoluble than those obtained with the sulphate, excepting only in the cases of the four cerite earths. These contain chlorine as well as sulphuric oxide, and they are sometimes at least formed when sulphate of luteocobalt is added to a solution containing the chlorides of metals of the cerium and yttrium groups. Sulphate of roseocobalt gives in general the same result as sulphate of luteocobalt, only the salts formed in this case are more soluble in both cold and hot water. Experiments with the sulphates of xanthocobalt and croceocobalt have not yet led to valuable results. Certain sulphates of the earths appear to give with sulphate of luteocobalt only hydroxides of the metals, $R(OH)_3$. In this case it seems more probable that a true double sulphate is at first formed and then decomposed, sulphuric acid being set free.

The following results may be of interest in this connection. A portion of earths from Fergusonite sent me by Dr. Shapleigh was converted into sulphates; the cerite earths had been separated by sodic sulphate, and the solution of the earths gave no further precipitate with this. A solution of sulphate of luteocobalt gave no precipitate with this solution in the cold, but on boiling a very abundant crystalline precipitate, insoluble or very slightly soluble in boiling water. The filtrate from these crystals gave only a small precipitate with ammonia, so that the luteocobalt salt must have contained almost all the earths other than the cerite earths. These are known to consist chiefly of yttria. The crystalline precipitate obtained as above by boiling, and insoluble in boiling water, dissolved completely in a large quantity of cold water. The nitrates of roseocobalt and luteocobalt give, in many cases at least, finely crystalline precipitates with the nitrates of the earths. In certain cases, white gelatinous precipitates of hydroxides are formed at the same time probably as in the case of the sulphates above cited, in consequence of the formation of double nitrates and their subsequent decomposition into free acid and hydroxide. This makes a new mode of differentiation which may prove to be of use, and to which I shall return hereafter. As an instance I may cite the case of the neutral nitrates of the gadolinite earths, from which the cerite earths have been separated by sodic sulphate. A strong solution of these nitrates gives with nitrate of roseocobalt, $Rc(NO_3)_3$, in a short time a bright orange highly crystalline and a dirty white gelatinous precipitate. Both contain earths. The same is

true for neutral nitrates from Samarskite, and from the cerite and monazite residues already mentioned. The nitrate of roseocobalt must be in excess. I have already stated that the action of the sulphates of roseocobalt and luteocobalt upon the sulphates of the earths closely resembles that of the alkaline sulphates. The advantage of using the cobaltamines consists, in part, in the fact that the double sulphates of these and the earths are highly crystalline and exceptionally well defined, and that they are in some cases at least very much less soluble than the alkaline double sulphates. The chief disadvantage is that the cobaltamines must be specially prepared for use, and that the most valuable of them — the sulphate of luteocobalt — is not easy to prepare in quantity and in a state of purity. Professor Morris Loeb has however found that sulphate of roseocobalt may be converted into sulphate of luteocobalt by heating with strong ammonia water under pressure, as for instance in sealed tubes; and as the sulphate of roseocobalt is easily prepared, this process is perhaps the best.

A solution of sulphate of luteocobalt gives a very insoluble yellow crystalline precipitate with sulphate of thoria, $Th(SO_4)_2$. It gives also slightly soluble precipitates with uranic sulphate, UO_2SO_4, and with a solution of ferric alum which has undergone dissociation by solution. This last precipitate appears to have the formula

$$Fe_2O \,.\, (SO_4)_2 + Lc_2(SO_4)_3.$$

It is my hope to be able to return to the subject in greater detail.

Relations of the Oxides to Lactic Acid. — A portion of the oxides obtained from Samarskite by Dr. Shapleigh after the cerite oxides had been separated by sodic sulphate was boiled with pure lactic acid, and gave an amethyst-red solution. On standing, this solution gave two kinds of crystals, which were very distinct and well defined. These were beautiful red flat prisms, and distinct bright yellow granular crystals. The quantity was too small to permit a more thorough examination, and I did not obtain the same result a second time with other Samarskite oxides. In one experiment, however, the solution of the oxides was deep orange, and after a time deposited crystals with a fine orange color.

The lactates of the cerite earths and of the Samarskite earths which have not been treated with potassic or sodic sulphate give beautiful white feathery crystals, which dissolve with difficulty in hot water.

Relations of Mercurous Nitrate and Mercuric Oxide to Cerite Earths. — A solution of mercurous nitrate gives in general no precipitate with neutral nitrates of the cerite earths. In one experiment, however, in

which I employed nitrates from a commercial oxalate, added a solution of mercurous nitrate, and then boiled with free mercuric oxide, the color of the oxide changed to a grayish tint. After filtering and washing, the filtrate was found to contain abundance of didymium (Nd and Ps). The precipitate after washing with boiling water was heated to redness in a platinum crucible, when a clear yellow powder remained. This dissolved in dilute nitric acid to a colorless liquid, which gave no didymium bands with the spectroscope. On adding water to the nitric acid solution a beautiful bright yellow crystalline powder was thrown down. When the oxides were treated with sulphuric acid a white crystalline mass was formed. Hot water gave with this a fine bright yellow crystalline precipitate. I did not obtain these results with any other samples of cerite oxalates. So far as I am aware no known earths exhibit the reactions with nitric and sulphuric acids above described.

Relations of the Samarskite Oxides to Acid Molybdates, and to Phospho-tungstates and Phospho-molybdates. — To determine whether any of the oxides contained in Samarskite were capable of forming complex inorganic acids, the following experiments were made with a bright yellow mixture of oxides prepared by Lawrence Smith's process with fluohydric acid. The quantity at my disposal was less than five grams, and I am not certain that the cerite oxides had been removed by sodic sulphate.

1. With 10 : 5 phospho-molybdate of ammonium. The mixed oxides dissolved very easily on boiling with solutions of the phospho-molybdate, giving a fine orange solution. The action of the solution of phospho-molybdate upon the oxides seemed to give instantly a crystalline mass, which on boiling with some excess of the phospho-molybdate dissolved. The solution gave beautiful orange-brown crystals, but after twenty-four hours the solution was clear, and had a fine rose-color. This solution gave no absorption bands with the spectroscope. With ammonic oxalate it gave a white crystalline precipitate with a clear rose-red solution. This on evaporation to dryness in a platinum vessel gave a rose-red mass, which when heated fused to a greenish mass. The white oxalate settled slowly. The orange crystalline salt dissolved almost completely in boiling water, but some yellow crystalline matter remained. On standing, the solution deposited crystals of a yellow salt.

2. With 14 : 6 molybdate of ammonium. A solution of 14 : 6 molybdate of ammonium (commonly written $7\,MoO_3 \,.\, 3\,(MH_4)_2O$) also readily dissolved the mixed oxides and gave a deep orange solution.

On standing twenty-four hours this gave bright yellow and afterwards very beautiful glittering orange-red crystals. The two kinds of crystals redissolved gave with mercurous nitrate a pale yellow flocky precipitate which on boiling and standing became bright yellow and highly crystalline. The least soluble crystals were also redissolved separately, and after twenty-four hours crystallized in beautiful prehnitic groups. The orange mother liquor from these crystals gave the reaction with mercurous nitrate mentioned above. It seems probable from the above that 14 : 6 molybdate of ammonium gives at least two distinct salts.

3. With 24 : 2 sodic phospho-tungstate. A solution of this salt also dissolved the Samarskite oxides very readily on boiling, giving a fine orange-red solution which soon deposited an abundance of yellow needles. These dissolved readily in hot water to a yellow solution with an orange tint. Yellow needles quickly formed in abundance. After an hour the still slightly warm mother liquor was poured off and allowed to stand. Two kinds of crystals separated, — very distinct rather large granular orange crystals in much the larger quantity, and very small granular yellow crystals differing much from the last in appearance. The two kinds of crystals were dissolved together in hot water, and after a time gave flocky masses of yellow crystals.

I did not succeed in obtaining the same results with other preparations of Samarskite oxides. This will not surprise those who have worked with the rare earths, and who have noticed the difference in the reactions which depends upon difference in the proportions of the mixed oxides. It has, I believe, escaped notice that the same occurs with mixtures of the different metals of the platinum group as long since shown by Claus.

The compounds with molybdic oxide and with phospho-molybdic and phospho-tungstic acids may prove to be only salts of the earths, and not of complex acids. They appear to deserve further attention as means of separation. As the minerals belonging to the same group with gadolinite resemble each other very closely in their physical characters, it is possible that the yellow oxides above mentioned were not prepared from Samarskite, but from some other mineral.

Analyses 1 to 46 and from 69 to 122 inclusive were made by Mr. Edward L. Smith; from 47 to 68 inclusive by Mr. Wm. J. Karslake. My grateful acknowledgments are due to both.

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